

Please amend the specification as follows:

Note: line numbering is in accordance with the substitute specification filed August 25, 2004.

Page 1, the paragraph at line 25:

In above mentioned Document A, ~~an~~ a useful photo-catalyst material to progress the splitting reaction of water to hydrogen and/or oxygen is illustrated, and many indications regarding hydrogen generating reaction by reduction of water or oxygen generating reaction by oxidization of water and a photo-catalyst for complete photo splitting reaction of water are mentioned. Further, said Document A refers to a photo-catalyst which loads a promoter such as platinum or NiO.

Page 1, the paragraph at line 32 to page 2, line 14:

However, a photo-catalyst illustrated in Document A is mainly the photo-catalyst which contains oxide as a non-metallic element. Further, since the width of the forbidden band of many solid photo-catalyst existing between valence band conduction band, namely, band gap energy is large (~~3eV~~) (3eV), it is hard to act by visible light of lower energy (energy: less than 3eV). In the meanwhile, almost all of conventional solid photo-catalyst whose gap energy is small and can generate electron and hole by visible light have a problem of photo corrosion under the reacting condition of photo splitting reaction of water. For

example, in the cases of CdS or Cu-ZnS, although the band gap is 2.4eV, since these are affected by oxidative photo corrosive action, the catalytic reaction is limited. While, almost all of the sun light which reaches to the surface of earth is visible light whose energy is small, and for the purpose to progress the various catalyst reaction, it is necessary to develop a photo-catalyst which is stable under the condition of photo catalytic reaction. However, unfortunately, there was no photo-catalyst to satisfy above mentioned requirement up to the present time.

Page 2, the paragraph at line 15:

As mentioned above, since almost all of sun light which can be utilized at the surface of earth is visible light, it was necessary to develop a photo-catalyst which is stable under various reaction conditions of oxidation and reduction. Almost all of the conventional stable photo-catalyst are the metal oxide, that is, containing oxide as a non metallic element. In the cases of these compounds, since the positional relationship between conduction band and valence band from energy view point is largely controlled by energy of valence electron (O2p) orbit of oxygen, band gap energy is large and can not generate photo-catalytic function by visible light. Since it was anticipated that the energy level of valence band is elevated when an element whose valence electron energy is higher than that of oxygen is reacted with metal and hybridize their valence electron orbits,

the inventors of the present invention considered if stable compound can be found out among these compounds under the photo-catalytic reaction condition, a novel photo-catalyst which acts by visible light will be able to be generated.

Page 2, the paragraph at line 31 to page 3, line 10:

Since the valence electron of nitrogen atom has higher energy than that of oxygen atom, the band gap energy of metal compound containing nitrogen atom can be ~~make~~ made smaller than that of metal oxide and a metal and metal compound which is bonded by adequate amount of nitrogen atoms becomes possible to generate an excitation electron and a hole by absorption of visible light of longer wave, and can be a photo-catalyst which acts by visible light. And the inventors of the present invention have continued intensive study to find out a compound which is stable under the reaction condition among these photo-catalysts, and found out that the compound composing of oxynitride containing at lease one transition element can fulfill the function of the photo-catalyst which ~~satisfy~~ satisfies the above mentioned condition, and already proposed as the invention which dissolved said problem (JP Application 2000-256681; filed on August 28, 2000). ~~Mostly~~ Most of these compounds have perovskite-type crystalline structure, and the stabilizing effect under said photo-catalyst reaction condition is conjectured to be caused by this structural feature.

Page 3, the paragraph at line 21:

The subject of the present invention is to provide a compound which is stable as a visible light active photo-catalyst having nitride bond of Ti(IV), further the object of the present invention is to provide a method for preparation of said compound. During the various considerations how to introduce a nitride bond into the compound containing Ti(IV), which has photo-catalytic activity, the inventors of the present invention found out that the introduction of nitride bond of Ti(IV) is possible when Ti(IV) contains F bond, and found out the synthesis of the compound containing Ti(IV) which has nitride bond by using compounds of  $\text{TiO}_a\text{N}_b\text{F}_c$  or  $\text{MeTiO}_a\text{N}_b\text{F}_c$ . And found that the obtained compound has a possibility to be a catalyst which is active by visible light, especially to be a catalyst which ~~generate~~ generates hydrogen or oxygen by photo splitting of water, thus the subject of the present can be accomplished. In the compounds of  $\text{TiO}_a\text{N}_b\text{F}_c$  or  $\text{MeTiO}_a\text{N}_b\text{F}_c$ , Me is an alkali earth metal such as Sr, c is 0.1 to 1, b is 0.1 to 1, desirably b 0.3, and a is a value to be decided in relation to b and c.

Page 4, the paragraph at line 10:

The first one of the present invention is a photo-catalyst containing titanium fluoride nitride comprising,  $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$  or a compound represented by  $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$  prepared by doping at least

one metal Me selected from the group consisting of alkali or alkaline earth metals on  $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$  (wherein. b is 0.1 to 1, c is 0.1 to 1 and a is a value to maintain Ti(IV) and is decided in relation to b and c.). Desirably, the present invention is the photo-catalyst containing titanium fluoride nitride, wherein  $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$  possesses ~~anatase~~ anatase structure and  $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$  possesses perovskite to anatase structure. Further desirably the present invention is the photo-catalyst containing titanium fluoride nitride to which at least one promoter selected from the group consisting of Pt, Ni and Pd is loaded.

Page 4, the paragraph at line 22:

The second one of the present invention is a photo-catalyst for water splitting containing titanium fluoride nitride comprising  $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$  or a compound represented by  $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$  prepared by doping at least one metal Me selected from the group consisting of alkali or alkaline earth metals on  $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ . (wherein. b is 0.1 to 1, c is 0.1 to 1 and a is a value to maintain Ti(IV) and is decided in relation with b and c.). Desirably, the second one of the present invention is a photo-catalyst for water splitting containing titanium fluoride nitride wherein  $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$  possesses ~~anatase~~ anatase structure and  $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$  possesses perovskite to ~~anatase~~ anatase structure. Further desirably the second one of the present invention is a photo-catalyst for water splitting containing titanium fluoride

nitride to which at least one promoter selected from the group consisting of Pt, Ni and Pd is loaded.

Page 4, the paragraph at line 35 to page 5, line 11:

The third one of the present invention is a method for preparation of a photo-catalyst represented by  $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$  (wherein a, b and c are same as to first one of the present invention) by baking titanium di-ammonium fluoride halide containing at least F represented by  $(\text{NH}_4)_2\text{TiF}_d\text{X}_{6-d}$  (wherein, d is 1-6) and ammonium halide by the ratio of equimolar or by the ratio of slightly excess of ammonium halide at the maximum temperature from 200°C to 500°C, desirably from 300°C to 450°C so as to form a starting material, then said starting material is nitrogenated by thermal synthesis in ammonia atmosphere containing from 0.02% to 10.00% of oxygen, air or water to ammonia by reduced mass to oxygen atom at the maximum temperature from 350°C to 700°C, desirably from 400°C to 600°C over than 5 hours.

Page 5, the paragraph at line 12:

The fourth one of the present invention is a method for preparation of a photo-catalyst represented by  $\text{SrTi(IV)O}_a\text{N}_b\text{F}_c$  wherein a, b and c are same as to the first one of the present invention by baking titanium di-ammonium fluoride halide containing at least F represented by  $\text{TiF}_x\text{X}_{6-x}$  and/or  $(\text{NH}_4)_2\text{TiF}_d\text{X}_{6-d}$

$(\text{NH}_4)_2\text{TiF}_d\text{X}_{6-d}$  (wherein x and d are 1-6) and at least one selected from the group consisting of SrO, SrOH and SrX so as to form a starting material or  $\text{SrTiF}_6$ , then said starting material or  $\text{SrTiF}_6$  is nitrogenated by thermal synthesis in ammonia atmosphere containing from 0.02% to 10.00% of oxygen, air or water to ammonia by reduced mass to oxygen atom at the maximum temperature from 350°C to 700°C over than 5 hours.

Page 7, the paragraph at line 30:

The present invention will be illustrated more in detail.  
 A. The photo-catalysts of the present invention can be obtained by satisfying the essential factors described in the claims.  
 As the compound having chemical composition of  $(\text{NH}_4)_2\text{TiF}_d\text{X}_{6-d}$   $(\text{NH}_4)_2\text{TiF}_d\text{X}_{6-d}$ , (wherein d is 1-6)  $(\text{NH}_4)_2\text{TiF}_6$   $(\text{NH}_4)_2\text{TiF}_6$  and  $(\text{NH}_4)_2\text{TiF}_2\text{XCl}_4$   $(\text{NH}_4)_2\text{TiF}_2\text{XCl}_4$  can be mentioned as the desirable one.

Page 8, the paragraph at line 22:

The X ray diffraction spectrum of the material after baking are shown in Fig.1. All diffraction peaks in Fig.1 are belonging to TiNF (refer to Paper: Angew. Chem. Int. Ed. Engle.27 (1988) No.7, p929-930) and the generation of TiNF is confirmed.  
 UV-Visible ray absorption characteristic curve of said material (obtained by diffuse reflectance spectrum) is shown in Fig.2.  
 From Fig.2, it ~~become~~ becomes clear that said material absorbs

visible light shorter than 600nm. From the result of elemental analysis, the ratio of Ti:O:N:F is 1:1.76:0.13:0.10 ( $\text{TiO}_{1.76}\text{N}_{0.13}\text{F}_{0.10}$ ).

Page 8, the paragraph at line 30 to page 9, line 8:

In Fig.3 the change of  $\text{H}_2$  generation amount by time lapse when 0.2g of material to which 3% of platinum is loaded is dispersed in  $0.310\text{dm}^3$  of 10vol.% methanol aqueous solution and visible light longer than 420nm is irradiated. 300w xenon lamp is used as the light source and the visible light shorter than 420nm is cut off by a cut off filter. As shown in Fig.3, it is understood that said material can generate hydrogen constantly from methanol aqueous solution by the irradiation of visible light longer than 420nm. Further, in Fig.4 the change of oxygen generation amount by time lapse, when 0.2g of above material is suspended into  $0.310\text{dm}^3$  of  $0.01\text{mol dm}^{-3}$   $\text{AgNO}_3$  aqueous solution and visible ray longer than 420nm is irradiated. The reaction is carried out by same condition mentioned above. From Fig.4, it ~~become~~ becomes clear that above mentioned material can generate oxygen from silver nitrate aqueous solution under irradiation of visible light longer than 420nm.

Page 9, the paragraph at line 25:

The X ray diffraction spectrum of the material after baking are shown in Fig.5. All diffraction peaks in Fig.5 are belonging



to TiNF (referred to afore mentioned Paper) and the generation of TiNF is confirmed. UV-Visible ray absorption characteristic curve of said material is shown in Fig.6. From Fig.6, it ~~become~~ becomes clear that said material absorbs visible light shorter than 600nm. From the result of elemental analysis, the ratio of Ti:O:N:F is 1:1.64:0.14:0.30.

Page 9, the paragraph at line 32 to page 10, line 10:

In Fig.7 the change of H<sub>2</sub> generation amount by time lapse when 0.2g of material to which 3wt% of platinum is loaded is dispersed in 0.310dm<sup>3</sup> of 10vol.% methanol aqueous solution and visible light longer than 420nm is irradiated. 300w xenon lamp is used as the light source and the visible light shorter than 420nm is cut off by a cut off filter. As shown in Fig.7, it is understood that said material can generate hydrogen constantly from methanol aqueous solution by the irradiation of visible light longer than 420nm. Further, in Fig.8 the change of oxygen generation amount by time lapse, when 0.2g of above material is suspended into 0.310dm<sup>3</sup> of 0.01mol/dm<sup>-3</sup> AgNO<sub>3</sub> aqueous solution and visible ray longer than 420nm is irradiated. The reaction is carried out by same condition mentioned above. From Fig.8, it ~~become~~ becomes clear that above mentioned material can generate oxygen from silver nitrate aqueous solution under irradiation of visible light longer than 420nm.

Page 10, the paragraph at line 28:

The X ray diffraction spectrum of the material after baking are shown in Fig.9. All diffraction peaks in Fig.9 are belonging to TiNF and the generation of TiNF is confirmed. UV-Visible ray absorption characteristic curve of said material is shown in Fig.10. From Fig.10, it ~~become~~ becomes clear that said material absorbs visible light shorter than 600nm. From the result of elemental analysis, the ratio of Ti:O:N:F is 1:1.74:0.13:0.14.

Page 10, the paragraph at line 34 to page 11, line 12:

In Fig.11 the change of hydrogen generation amount by time lapse when 0.2g of material to which 3wt% of platinum is loaded is dispersed in 0.310dm<sup>3</sup> of 10 vol.% methanol aqueous solution and visible light longer than 420nm is irradiated. 300w xenon lamp is used as the light source and the visible light shorter than 420nm is cut off by a cut off filter. As shown in Fig.11, it is understood that said material can generate hydrogen constantly from methanol aqueous solution by the irradiation of visible light longer than 420nm. Further, in Fig.12 the change of oxygen generation amount by time lapse, when 0.2g of above material is suspended into 0.310dm<sup>3</sup> of 0.01mol dm<sup>-3</sup> AgNO<sub>3</sub> aqueous solution and visible ray longer than 420nm is irradiated. The reaction is carried out by same condition mentioned above. From Fig.12, it ~~become~~ becomes clear that above mentioned material can generate oxygen from silver nitrate aqueous solution under irradiation of

visible light longer than 420nm.

Page 11, the paragraph at line 31 to page 12, line 1:

The X ray diffraction spectrum of the material after baking are shown in Fig.13. All diffraction peaks in Fig.13 are belonging to TiNF and the generation of TiNF is confirmed.

UV-Visible ray absorption characteristic curve of said material is shown in Fig.10. From Fig.10, it ~~become~~ becomes clear that said material absorbs visible light shorter than 600nm. From the result of elemental analysis, the ratio of Ti:O:N:F is 1:1.45:0.30:0.20.

Page 12, the paragraph at line 2:

In Fig.15 the change of hydrogen generation amount by time lapse when 0.2g of material to which 3wt% of platinum is loaded is dispersed in 0.310dm<sup>3</sup> of 10 vol.% methanol aqueous solution and visible light longer than 420nm is irradiated. 300w xenon lamp is used as the light source and the visible light shorter than 420nm is cut off by a cut off filter. As shown in Fig.15, it is understood that said material can generate hydrogen constantly from methanol aqueous solution by the irradiation of visible light longer than 420nm. Further, in Fig.16 the change of oxygen generation amount by time lapse, when 0.2g of above material is suspended into 0.310dm<sup>3</sup> of 0.01mol dm<sup>-3</sup> AgNO<sub>3</sub> aqueous solution and visible ray longer than 420nm is irradiated. The reaction is

carried out by same condition mentioned above. From Fig.16, it ~~become~~ becomes clear that above mentioned material can generate oxygen from silver nitrate aqueous solution under irradiation of visible light longer than 420nm.

Page 12, the paragraph at line 20 to page 13, line 1:

Titanium fluoride  $\text{TiF}_4$  (0.9g) and strontium fluoride  $\text{SrF}_4$  (0.6g) were mixed together in Ar atmosphere and sealed in a golden tube. This golden tube was further sealed in a Pyrex glass tube in vacuum condition and the temperature was elevated by temperature-programming speed of 10K/minute, then the temperature was maintained at 450°C for 8 hours. After that cooled down to room temperature and  $\text{SrTiF}_6$  was synthesized. The obtained  $\text{SrTiF}_6$  was set under ammonia stream containing oxygen (ammonia flow rate:  $0.4\text{dm}^3\cdot\text{min}^{-1}$ , oxygen flow rate:  $0.4\text{cm}^3\cdot\text{min}^{-1}$ ) and the temperature was elevated to 673K by temperature-programming speed of 10K/minute under ammonia stream of  $40\text{dm}^3/\text{min}$  flow rate and maintained for 5 hours by this temperature. After that the temperature was cooled down to room temperature and  $\text{SrTiONF}$  material was synthesized. According to the elemental analysis results, the ratio of Sr:Ti:O:N:F was 1:2.35:0.30:0.40. Pt, which is a promoter, was deposited on a catalyst by dispersing platonic chloride  $\text{HPtCl}_6$  in following reaction solution then photo ~~electrodepositing~~ electrodepositing. Impregnated amount of the promoter can be adjust in the range from 0.1 to 10 weight %.

Page 13, the paragraph at line 2:

UV-Visible ray absorption characteristic curve of said material is shown in Fig.17. From Fig.17, it ~~become~~ becomes clear that said material absorbs visible light shorter than 600nm. In Fig.18 the change of hydrogen generation amount by time lapse when 0.2g of material to which 1wt% of platinum is loaded is dispersed in 0.200dm<sup>3</sup> of 10 vol.% methanol aqueous solution and visible light longer than 420nm is irradiated. 300w xenon lamp is used as the light source and the visible light shorter than 420nm is cut off by a cut off filter. As shown in Fig.18, it is understood that said material can generate hydrogen constantly from methanol aqueous solution by the irradiation of visible light longer than 420nm. Further, in Fig.19 the change of oxygen generation amount by time lapse, when 0.2g of above material is suspended into 0.200dm<sup>3</sup> of 0.01mol/dm AgNO<sub>3</sub> aqueous solution and visible ray longer than 420nm is irradiated. The reaction is carried out by same condition mentioned above. From Fig.19, it ~~become~~ becomes clear that above mentioned material can generate oxygen from silver nitrate aqueous solution under irradiation of visible light longer than 420nm. From above mentioned results, it is confirmed that SrTiONF has an ability to reduce proton to hydrogen and to oxidize water to oxygen by visible light which has longer wave length than 420nm.

Page 13, the paragraph at line 28:

The X ray diffraction spectrum of said material is shown in Fig.20. In Fig.20, diffraction peaks of ~~anatase~~ anatase phase and rutile phase can be observed. UV-Visible ray absorption characteristic curve of said material is shown in Fig.21. From Fig.21, it ~~become~~ becomes clear that said material absorbs only UV light shorter than 400nm, and does not absorb visible light.

Page 14, the paragraph at line 23:

Strontium titanate  $\text{SrTiO}_3$  on the market was used. Pt, which is a promoter, was deposited on a catalyst by dispersing platinum chloride  $\text{H}_2\text{PtCl}_6$  in following reaction solution then photo ~~electrodepositing~~ electrodepositing. Impregnated amount of the promoter can be adjust in the range from 0.1 to 10 weight %.

Page 15, the paragraph at line 2:

Strontium titanate  $\text{SrTiO}_3$  on the market was set under ammonia  $\text{NH}_3$  stream of flow rate 40dm/min, and the temperature was elevated to  $400^\circ\text{C}$  (673K) by temperature-programming speed of 10K/min and maintained this temperature for 5hours, then the temperature was cooled down to room temperature in Ar atmosphere and  $\text{SrTi}(\text{OH})_x$  material was synthesized. Pt, which is a promoter, was deposited on a catalyst by dispersing platinum chloride  $\text{H}_2\text{PtCl}_6$  in following reaction solution then photo ~~electrodepositing~~ electrodepositing. Impregnated amount of the

promoter can be adjusted in the range from 0.1 to 10 weight %.

Page 15, the paragraph at line 11:

The X ray diffraction spectrum of said material after baking is shown in Fig.26. Diffraction peaks in Fig.26 are confirmed to belong to  $\text{SrTiO}_3$ . UV-Visible ray absorption characteristic curve of said material is shown in Fig.27. From Fig.27, it ~~become~~ becomes clear that said material absorbs visible light shorter than 600nm. However, in longer wave length side, absorption which can be guessed to originate to  $\text{Ti}^{3+}$  generated by reduction is observed. Same as to Example 1, reactions were carried out under visible ray irradiation, however, generations of  $\text{H}_2$  and  $\text{O}_2$  were not observed.